MÖSSBAUER SPECTROSCOPY OF PHASE AND CRYSTAL-CHEMICAL STATES OF IRON OXIDES IN CERAMIC BRICK

N. D. Yatsenko,[1] K. A. Verevkin,[1] and A. P. Zubekhin[1]

The phase state of iron oxides in ceramic brick, obtained with reductive calcination, has been determined by Mössbauer spectroscopy.

Key words: Mössbauer spectroscopy, phase composition, iron oxide, degree of reduction, ceramic brick.

Quality — physical operational and aesthetic-user properties meeting strict modern requirements — is the most important factor determining the competitiveness of products.

In residential and industrial construction, one of the widely used building materials is ceramic brick, whose physical properties are determined by strength and frost-resistance while the aesthetic-architecture properties are determined by its color. However there is still no clear picture of its phase composition and the essence of the color change as a function of the composition of the clayey raw material and the calcination conditions. In this connection, Mössbauer spectroscopy (MS) studies of the phase state of iron oxides in ceramic brick, obtained from various high-iron clays at calcination temperature 1000°C in a reducing medium. Clays from the following deposits were investigated: Karkinskoe (Kirovo-Chepetsk), Belkinskoe (Kaliningrad), Verkh-Tulinskoe (Novosibirsk), and Obidimskoe (Tula).

The compositions of the ceramic masses for obtaining brick are presented in Table 1.

The ceramic mixes are characterized by the following chemical composition (Table 2): elevated content of oxides Fe_2O_3 in the range 5.04 – 6.46%[2] by weight and substantial fluctuations of SiO_2 from 55.42 to 74.63%, which in the latter case attests to an elevated content in clay of free silica SiO_2 in the form of sand.

To prepare ceramic mixes all materials were comminuted in a laboratory ball mill to particle size 0.8 mm. After they were measured out and mixed to obtain a plastic mix with moisture content 18%, samples in the form of $100 \times 60 \times 10$ mm slabs were formed from them. The indicators of the post-calcination properties of the brick samples are presented in Table 3.

[1] Southern Russia State Technical University (Novocherkassk Polytechnical Institute), Novocherkassk, Russia.

[2] Here and below — content by weight.

TABLE 1. Mix Composition

Deposit of ceramic mix	Content by weight, %		
	clay	argillite	sand
Karkinskoe	40	40	20
Belkinskoe	80	–	20
Obidimskoe	80	–	20
Verkh-Tulinskoe	80	–	20

TABLE 2. Chemical Compositions of Ceramic Mixes

Deposit of ceramic mix	Content by weight, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	others
Karkinskoe	67.20	13.38	6.46	1.06	2.99	1.97	1.23	0.012	4.70
Belkinskoe	55.42	15.04	6.32	5.76	2.79	3.90	0.37	0.06	9.20
Obidimskoe	74.63	11.14	5.04	0.69	0.91	1.86	0.37	0.13	4.30
Verkh-Tulinskoe	66.92	13.90	6.81	1.22	1.86	2.21	0.77	0.01	5.02
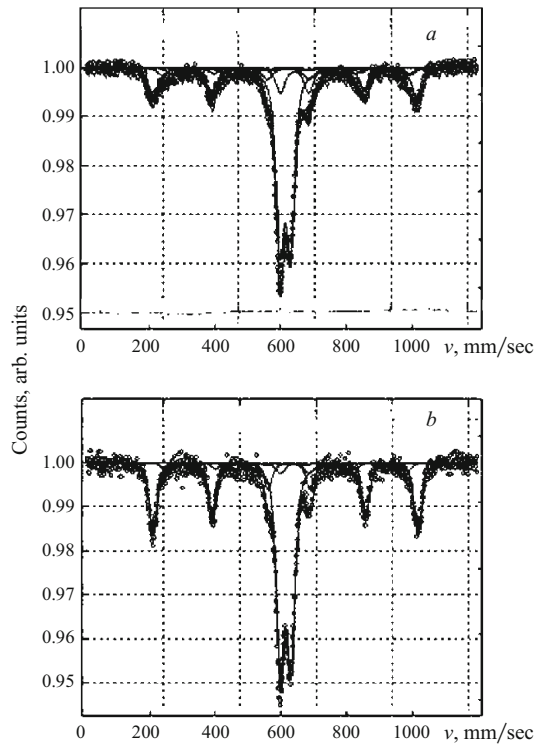
Fig. 1. Mössbauer spectra of samples of Karkin ceramic brick: *a*) surface layer; *b*) in volume.
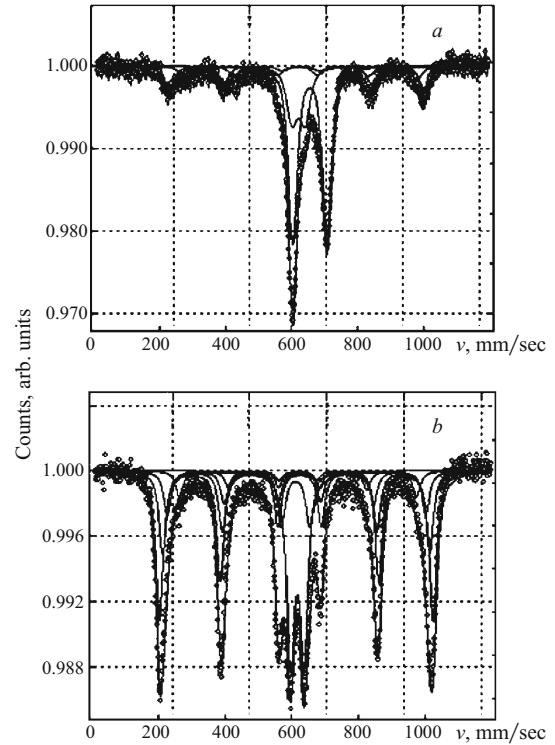

Fig. 2. Mössbauer spectra of samples of Verkh-Tulinskoe ceramic brick: *a*) surface layer; *b*) in volume.

Analysis of the results of the present investigations shows that the low values of the indicator of the post-calcination properties of samples of Obidimskoe samples are explained by the high content of free silica SiO_2 in the ceramic mix — sand (see Table 2), which resulted in inadequate sintering.

The substantial change in the color of the samples from orange-red to dark, almost black, is of greatest interest. It is well known [1, 2] that red and red-brown colors of ceramic brick with oxidative calcination are due to the content of the free mineral hematite á-Fe_2O_3 in the brick; this mineral is present in the clayey raw material itself or it forms during the decomposition and oxidation of iron-containing phases.

When a reducing gas atmosphere is created in the furnace or reducing substances are present in the ceramic mixes, Fe_2O_3 is reduced to Fe_3O_4 or FeO, which gives rise to a change of color to black depending on the degree of reduction and the ratio of the quantities of the iron oxides as well as on the formation of independence iron-containing phases of the type $FeFe_2O_3$, Fe_2SiO_4, $2CaO \cdot Fe_2O_3$, which have a very low reflection coefficient.

To solve this important problem of chromaticity and whiteness of ceramic and other silicate decorative materials Mössbauer spectroscopy, which is a high-precision, high-accuracy, and selective method, was applied to iron ions in the most different valence, coordination, and phase states in the structures of crystalline and glassy substances.

The results of these studies made it possible to determine that the Mössbauer spectra of the Karkin and other samples are similar, while the Mössbauer spectrum of the Verkh-Tulinskoe sample shows some differences (Figs. 1 and 2).

The Mössbauer spectra consist of a superposition of the sextets 1, 2, 3, and 4 and doublets 1, 2, whose parameters are: δ — the chemical shift, determining the degree of oxidation (valence) of the Mössbauer atoms, their coordination and the character of the bond with the surrounding atoms (ions); the quadrupole splitting ΔE_Q which depends on the degree of oxidation and coordination of the atoms as well as the degree of distortion of the symmetry and environment; H_{eff} — the

TABLE 3. Properties of Brick Samples

Indicator	Deposit of ceramic mix			
	Karpin-skoe	Belkin-skoe	Obidim-skoe	Verkh-Tu-linskoe
Shrinkage, %:				
during calcination	2.0	1.9	1.0	0.1
total	8.2	6.8	6.7	4.1
Water absorption, %	9.6	10.8	10.5	13.1
Tile density, kg/m³	2100	1980	2050	1960
Strength, MPa:				
in compression	76.8	73.6	58.5	72.0
in bending	14.3	12.4	10.5	9.6
Color	Dark-grey	Black	Black	Black

TABLE 4. Parameters of Mössbauer Spectra and Iron Phases

Values of the Mössbauer parameters of the samples	Elements of the Mössbauer spectra									
	surface (spectrum *a*)					in volume (spectrum *b*)				
	δ, mm/sec	ΔE_Q, mm/sec	H, kOe	S, arb. %	Fe state	δ, mm/sec	ΔE_Q, mm/sec	H, kOe	S, arb. %	Fe state
Karkinskoe deposit (see Fig. 1)										
Spectrum 1	0.7333	− 0.1911	498.3	25.71	Fe_2O_3	0.5592	− 0.2116	500.1	38.65	Fe_2O_3
Spectrum 2	0.7333	0.0000	460.0	6.45	Fe_3O_4	0.5592	0.0639	457.5	4.19	Fe_3O_4
Spectrum 3	0.7333	0.0000	449.2	5.61	Fe_3O_4	0.5592	− 0.0934	356.6	1.79	Fe_3O_4
Doublet 1	0.5942	0.6351	–	53.6	Fe^{3+}	0.5942	0.6610	–	52.19	
Doublet 2	0.6424	1.7362	–	8.62	Fe^{2+}	0.6424	1.7467	–	3.18	Fe^{2+}
Verkh-Tulinskoe deposit (see Fig. 2)										
Spectrum 1	0.7240	− 0.0421	479.9	16.93	Fe_3O_4	0.5181	− 0.2061	508.2	35.10	Fe_2O_3
Spectrum 2	0.7244	− 0.0049	436.2	9.06	Fe_3O_4	0.5181	− 0.2159	496.2	19.32	Fe_2O_3
Spectrum 3	–	–	–	–	–	0.5181	0.0123	440.8	6.13	Fe_2O_3
Spectrum 4	–	–	–	–	–	0.5181	− 0.1545	480.3	10.43	Fe_2O_3
Doublet 1	0.7759	0.7813	–	18.72	Fe^{3+}	0.5659	0.2312	–	6.78	Fe^{3+}
Doublet 2	0.6574	2.0719	–	52.77	Fe^{2+}	0.5659	0.7834	–	22.24	Fe^{3+}

intensity of the internal magnetic field arising with the formation of the magnetically ordered phases (crystals) such as α-Fe_2O_3, Fe_3O_4, Fe_2SiO_4, and others; G — the linewidth determined by the properties of the nuclei or S — the area of the spectrum, proportional to the content of the Mössbauer ions (atoms), which determine the phase composition and the crystal-chemical state in this case of ions, oxides, and compounds of iron.

Table 4 gives the parameters of the Mössbauer spectra which were used as basis for performing the diagnostics of iron containing phases.

The following iron-containing phases were differentiated in the Karkin brick. In the surface layer the spectral fraction of reduction of Fe_2O_3 is represented in the form of the magnetite phase $FeFe_2O_4$ (Fe_2O_3) — 12.06% and fayalite Fe_2SiO_4 — 8.62%, i.e., about 20% in all. The experimental linewidths and the values of the internal magnetic fields indicate the presence of not pure iron oxides but rather solid solutions based on them. In addition, Fe^{3+} ions can be present in the structure of the glass phase.

As the contents of Fe_3O_4 and Fe^{2+} show, the degree of reduction of Fe_2O_3 in the interior volume of the glass does not exceed 9.0%.

In the same made from the Verkh-Tulinskoe mix the degree of reduction of Fe_2O_3 in the surface layer is about 80% and crystalline phase containing Fe^{2+} — magnetite $FeFe_2O_4$ and fayalite Fe_2SiO_4 — are formed, while Fe^{3+} ions in the form of hematite α-Fe_2O_3 also enter into the structure of the glass phase.

Practically all of the iron in the interior volume of a sample is contained in a trivalent state, i.e. is does not undergo reduction.

The different degree of reduction of iron on the surface and in the volume of the brick can be explained by the different crystal-chemical state of the iron-containing compounds in the raw materials as well as the inadequate efficiency of the reducing medium because of the density of the calcined intermediate produce (green part).

In summary, the data obtained for the degree of reduction of iron oxides Fe_2O_3 to Fe_3O_4 and Fe^{2+} correlated completely with the color of the brick. The presence elevated quantities of Fe_3O_4, which is black, in the structure of the brick and the simultaneous presence of Fe^{3+} and Fe^{2+}, which form a chromophoric group $Fe^{3+} – O – Fe^{2+}$, giving rise to strong light absorption and, correspondingly, to a sharp decrease of the reflection coefficient of the materials, impart to the brick a dark, up to black, color. This dependence is used in the technology for producing brick for decorative articles in architectural-building design. In addition, the reducing medium intensifies the sintering process in brick by increasing the amount of melt and decreasing its viscosity.

REFERENCES

1. A. P. Zubekhin and S. P. Golovanova, "Theoretical principles of decolorizing cement clinker and red-burning ceramic with different content of iron oxides," in: *Bull. of the Nats. Tech. University "KhPI," Topical Edition "Chemistry and Chemical Technology"* [in Russian], NTU "KhPI", Kharkov (2004), No. 33.
2. A. P. Zubekhin, S. P. Golovanova, N. D. Yatsenko, and A. S. Deeva, "Physical-chemical and spectroscopic principles of decolorizing iron-containing silicate materials," *Tekh. Tekhnol. Silikatov*, No. 4, 41 – 43 (2007).